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Properties of GdFeAl ternary compound in two crystallographic structures

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Properties of the GdFeAl compounds crystallizing in the cubic $MgCu_2$-type structure as well as in hexagonal $MgZn_2$-type structure have been compared. The electrical resistivity, ac susceptibility and magnetization in function of temperature revealed relatively high magnetic ordering temperature, ca. 200 K. The differences in magnetization were observed for samples crystallizing in two different crystallographic structures. The magnetic moments measured at 4.2 K and up to140 kOe are very far from the value of the magnetic moment of a free Gd ion. The magnetic moments of cubic and hexagonal phases are 1.1 μ_B and 1.7 μ_B, respectively.

Key words: *rare earth transition metal compounds; lattice parameters; magnetization; electrical resistivity*

1. Introduction

Magnetic refrigeration technology is at present one of the most studied research issues in advanced refrigeration systems [1]. Magnetic refrigeration, based on magnetocaloric effect (MCE), offers the prospect of an energy-efficient and environment friendly alternative to the common vapour-cycle refrigeration technology in use today [2, 3]. Materials based on gadolinium are prospective for applications in magnetic refrigeration cycles. Recently, interest in other magnetocaloric materials such as e.g. RM_2 (M = Al, Co, Ni), $MnFe(P_{1-x}As_x)$, $Mn(As_{1-x}Sb_x)$, $La(Fe_{13-x}Si_x)$ has also been reported [4, 5]. These new materials have important significance for magnetic cooling.

Recently, magnetic and magnetocaloric properties of GdFeSi have been investigated as a part of research concerning the development of new materials for magnetic refrigeration devices [6]. GdFeSi polycrystalline sample crystallizes in the Cu_2Sb type structure and orders feromagnetically at 118 K. However, a high magnetic field employed together with the large temperature span for the refrigerant capacity integration prevents any industrial applicability. The intermetallic ternary compounds of the RTX

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type, consisting of a rare earth R, transition metal T and a p element X exhibit an enormously rich variety of crystallographic structures and magnetic properties. Some of these compounds could exist in various crystallographic structures. The well known example is GdPdAl (TiNiSi or ZrNiAl) [7]. Usually, the type of assumed structure depends on the way in which it was synthesized. A well known example of such a compound is GdPdAl which crystallizes in TiNiSi type structure, when cooled slowly or in ZrNiAl-type structure, when quenched [7]. Presence of high pressure during the crystallization can change the ZrNiAl-type structure of RCuAl and RNiAl to a more densely packed $MgCu_2$ structure (the former compound) and to $MgZn_2$ type (the latter one) of the Laves phase [8]. Recently, properties of GdPdX (X = Al, Si, Ga, Ge, In, Si) compounds have been extensively examined [9]. The magnetic ordering temperatures of the GdPdX compounds are close 30 K, except for GdPdIn. This latter has much higher ordering temperature of about 100 K.

Due to the lack of information relevant to the intermetallic compound GdFeAl, a complete research has been performed. In this paper, we report differences between the crystal structures and magnetic properties of two forms of the GdFeAl compound. Moreover, the electrical resistivity and ac magnetic susceptibility measurements for the cubic phase of the GdFeAl are presented.

2. Experimental

Polycrystalline GdFeAl intermetallic compounds were prepared by arc melting on a cool copper plate under the argon atmosphere from the stoichiometric amounts of high purity constituents. The obtained samples were divided into two parts, then one of them was annealed at 1000 K for one day and then cooled slowly, and the other ones were annealed and quenched. The obtained compounds were identified by the X-ray power diffraction with the CuK_α radiation using a Siemens D-5000 diffractometer. For the quenched sample the lattice parameters were obtained at room temperature, while for the annealed one the lattice constants were determined on decreasing the temperature from 300 K to 10 K and then increasing to 300 K again.

Measurements of the magnetization were performed in a static magnetic field up to 140 kOe at temperatures from 4.2 to 300 K. The electrical resistivity measurements were performed by a conventional four-point technique using 300 mA dc current in the temperature range 4.2–300 K. The ac magnetic susceptibility was measured at the frequency of 1 kHz in the temperature range 4.2–300 K. The ac magnetic field of 150 mOe was applied.

3. Results and discussion

The X-ray diffraction examination confirmed the hexagonal $MgZn_2$ type of the crystal structure for the annealed and quenched sample, and revealed the cubic $MgCu_2$

type of the structure in the case of the annealed and slowly cooled sample. The values of the lattice constants obtained at room temperature and compared to the literature ones are collected in Table 1.

Table 1. Lattice parameters of GdFeAl

GdFeAl	Lattice constant *a* [Å]	Lattice constant *c* [Å]	Structure type
Quenched	5.442	8.831	hexagonal, $MgZn_2$, *P*63/*mmc*, this work
Quenched	5.445	8.8809	hexagonal, $MgZn_2$, *P*63/*mmc* [11]
Annealed	7.724	–	cubic, $MgCu_2$, *F*d3*m*, this work
Annealed	7.750	–	cubic, $MgCu_2$, *F*d3*m* [12]

In the hexagonal $MgZn_2$ phase, Gd atoms are situated at 4*f* positions while Fe and Al atoms are placed randomly at 6*h* and 2*a* positions, the distance between the nearest Gd atoms being equal to 3.313 Å. In the cubic $MgCu_2$ phase, each Gd atom, placed at the 8*a* position, has four Gd neighbours at the a distance of 3.345 Å. The Fe and Al atoms are distributed randomly at 16*d* positions. The Laves phases are mainly the electron compounds and the type of their crystallographic structure depends not only on the atomic radii of the component elements but also on the electron concentration. For the ternary aluminides $R(T_xAl_{1-x})_2$, when the concentration *x* decreases from 1 to 0 and simultaneously the concentration of electrons per atom increases from 1 to 3, the structure changes from the type of $MgCu_2$ to $MgZn_2$ and back to $MgCu_2$ type [10]. The cubic phase is stable for low electron concentrations, smaller than 1.8*e*/*a* and for the concentrations higher than 2.3*e*/*a*. The GdFeAl equiatomic compound has two electrons per atom. This seems that this compound is close to the electron concentration limit of the occurrence of the hexagonal phase and can crystallize also in the cubic structure.

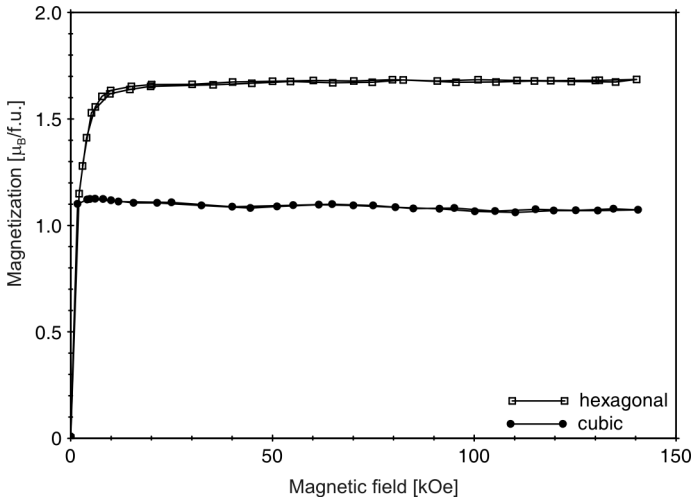

Fig. 1. Magnetization in function of magnetic field (at 4.2 K) of the cubic and hexagonal phases of the GdFeAl

The magnetization curves obtained at 4.2 K in high magnetic fields (up to 140 kOe) are shown in Fig. 1. The saturation in a very low magnetic field is observed. The magnetic moments of the cubic and hexagonal phases are $1.1\mu_B$ and $1.7\mu_B$, respectively. The observed magnetic moments are very far from the saturation value of 7 μ_B for the free Gd^{3+} ion. In GdNiAl and GdCoAl as well as in GdCuAl compounds the saturation magnetic moments were close to 6 μ_B [13]. In the more densely packed $MgZn_2$, the distance to nearest neighbours is smaller than in the cubic lattice. It results in a better ordering of Fe moments and in a larger resultant magnetic moment observed in the experiment.

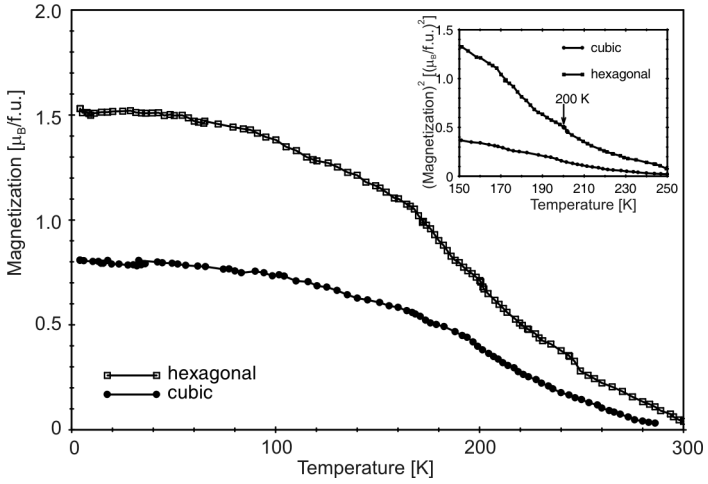

Fig. 2. Temperature dependence of magnetization of the cubic and hexagonal phases of the GdFeAl; inset: temperature dependence of the quadratic magnetization

Figure 2 presents the dependence of the magnetization on temperature of the hexagonal and cubic phases of GdFeAl. The order–disorder transition temperatures are not clearly visible for hexagonal and cubic phases. For the hexagonal phase of GdFeAl, a small inflection about 200 K is observed. However, further investigations are required to verify a possible presence of this magnetic transition.

The thermal dependence of the electrical resistivity of the GdFeAl compound with the cubic structure is shown in Fig. 3. A transition related to the order-disorder transition is visible at 225 K. A fitting of the electrical resistivity data in both studied directions according to the formula:

$$\rho(T) = \rho_0 + AT^2$$

in the temperature range from 0 K to 90 K yielded the value of A equal to 4.5×10^{-6} $\mu\Omega\cdot m\cdot K^{-2}$ and of the residual resistivity $\rho_0 = 1.58$ $\mu\Omega\cdot m$. In the case of GdFeAl, the magnetic properties are due to Gd 4f localized magnetic moments and to the Fe 3d band, which is not filled, contrary to Ni and Co 3d bands in GdNiAl and GdCoAl compounds [14].

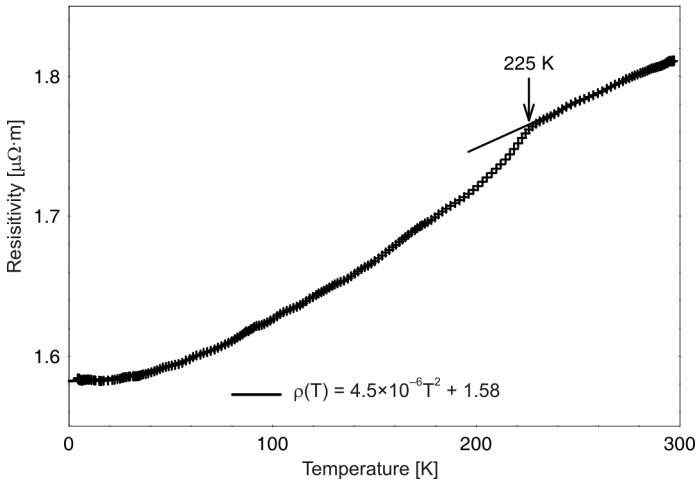

Fig. 3. Temperature dependence of the electrical resistivity of the GdFeAl cubic phase

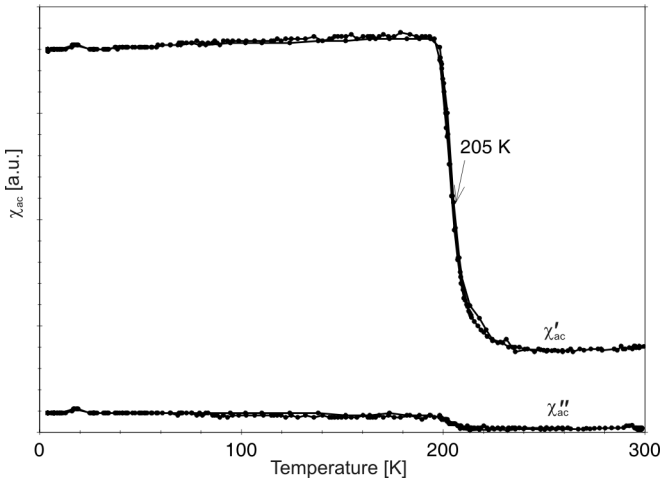

Fig. 4. Temperature dependence of the dispersion part of the ac magnetic susceptibility of the cubic phase of the GdFeAl

The temperature dependence of the ac magnetic susceptibility studied in the temperature range 4.2–300 K shows the transition for cubic phase of the GdFeAl (Fig. 4) at the relatively high temperature T_C = 205 K.

4. Conclusions

The GdFeAl compound can crystallize in the hexagonal $MgZn_2$ type or in the cubic $MgCu_2$ type structures depending on the thermal treatment. The magnetization, electrical resistivity and ac susceptibility measurements provide evidence for a mag-

netic transition at about 200 K. The GdFeAl compounds contain the Gd atoms with localized 4f magnetic moments together with the Fe 3d atoms and non-magnetic aluminum. The influence of iron on the properties of the compounds under investigation needs further examinations.

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